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CROSSLINKING OF PERFLUOROCARBON POLYMERS

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This technical report has been reviewed and is approved for publication.



R. C. Evers
Project Engineer

FOR THE DIRECTOR



R. L. Van Deusen, Chief
Polymer
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identified. The presence of aromatic substituents resulted in perfluoroalkylether chain activation.

A functional epoxide precursor, 4-bromoheptafluorobutene-1 was prepared and the procedure for its oxidation to the epoxide was optimized.

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FOREWORD

This report was prepared by Ultrasystems, Inc., Irvine, California under Contract No. F33615-76-C-5054, "Crosslinking of Perfluorocarbon Polymers", and covers work performed during the period 16 February 1976 through 16 February 1977. The Contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 04, "New Organic and Inorganic Polymers". The investigations were carried out by R. H. Kratzer, J. Kaufman, T. I. Ito, J. H. Nakahara and K. L. Paciorek, Project Manager. This contract was administered under the direction of the Air Force Materials Laboratory, Polymer Branch, Dr. R. C. Evers (AFML/MBP), Project Engineer.

TABLE OF CONTENTS

I	INTRODUCTION	1
II	DISCUSSION	2
	1. Synthesis of Functional Monomers	2
	2. Crosslinking Investigations of Nonfunctional Systems	5
III	EXPERIMENTAL DETAILS AND PROCEDURES	27
	1. General	27
	2. Material Purification and Characterization	27
	a. Perfluorotetrahydrofuran	27
	b. Triphenylphosphine	28
	c. Perfluoro(methylcyclohexane)	30
	d. Tetraphenyldiphosphine	30
	e. Freon E-7 (c) (ELO66-55)	30
	3. Monomer and Model Compound Synthesis	33
	a. Preparation of $(CF_3)_2CFO(CF_2)_4^-$ $OCF(CF_3)_2$	33
	b. Preparation of bis(pentafluorophenyl)- chlorophosphine	34
	c. Preparation of Tetrakis(pentafluoro- phenyl)diphosphine	35
	d. Preparation of n-Perfluoroheptene-1	36
	e. Epoxidation of n-Perfluoroheptene-1	37
	i) Using 30% H_2O_2	37
	ii) Using 60% H_2O_2	38
	f. Preparation of $Br(CF_2CF_2)_2CO_2Me$	38
	g. Preparation of $Br(CF_2CF_2)_2CO_2Na$	40
	h. Preparation of $BrCF_2CF_2CF=CF_2$	41
	4. Crosslinking Studies	42
IV	REFERENCES	44

LIST OF ILLUSTRATIONS

1	GC-MS Trace of Perfluorotetrahydrofuran	29
2	GC-MS Trace of Perfluoro(methylcyclohexane)	31
3	DTA of Freon E-7 (c) (ELO66-55)	32

LIST OF TABLES

1	Summary of Thermal Crosslinking Investigations	9
2	Volatile Products Obtained on Interaction of Triphenylphosphine and Perfluoro(methylcyclohexane) .	11
3	Products Obtained on Interaction of Tetraphenyl- diphosphine and Perfluoro(methylcyclohexane) at 300°C for 24 hr	12
4	Products Obtained on Interaction of Tetraphenyl- diphosphine and Perfluoro(methylcyclohexane) at 250°C for 113 hr.	14
5	Products Obtained on Interaction of Tetraphenyl- diphosphine and $(CF_3)_2CFO(CF_2)_4OCF(CF_3)_2$ at 250°C for 42 hr	15
6	Products Obtained on Interaction of Tetraphenyl- diphosphine and $(CF_3)_2CFO(CF_2)_4OCF(CF_3)_2$ at 300°C for 24 hr	16
7	Gas Chromatographic Analysis of ELO66-55, Freon E-7(c) Fluid	18
8	Summary of ELO66-55, Freon E-7(c) Fluid Reactions . .	18
9	Gas Chromatographic Analysis of ELO 66-55, Freon E-7(c) Fluid (Area/ μ l after Various Heat Treatments) . .	19
10	Gas Chromatographic Analysis of ELO 66-55, Freon E-7(c) Fluid (Area as Percent of Largest Peak after Various Heat Treatments)	19

LIST OF TABLES -- Continued

11	Products Obtained on Interaction of Potassium Diphenylphosphide with Perfluoro(methylcyclohexane) at 154°C	21
12	Products Obtained on Interaction of $\text{RCF}(\text{CF}_3)-$ $[\text{OCF}_2\text{CF}(\text{CF}_3)]_4\text{OC}_3\text{F}_7$ and $(\text{C}_6\text{H}_5)_4\text{P}_2$	24
13	Summary of $n\text{-C}_7\text{F}_{15}\text{COONa}$ Pyrolysis Experiments	36
14	Ion Fragments and Intensities Relative to Base Peak of n -Perfluoroheptene Oxide	39
15	Effect of Reaction Period on Completeness of the Epoxidation Process	39
16	Ion Fragments and Intensities Relative to Base Peak of $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$	42

SUMMARY

Crosslinking investigations of perfluorinated systems employing metalloid compound initiated thermal cure and a functional epoxide approach are reported. Using triphenylphosphine and tetraphenyl-diphosphine at temperatures up to 300°C , no reaction was observed with perfluoroalkylethers; with perfluoro(methylcyclohexane) some fluorine abstraction took place but no coupling products could be identified. The presence of aromatic substituents resulted in perfluoroalkylether chain activation.

A functional epoxide precursor, 4-bromoheptafluorobutene-1 was prepared and the procedure for its oxidation to the epoxide was optimized.

I. INTRODUCTION

Synthetic as well as natural gums must be crosslinked to three-dimensional networks in order to impart good viscoelastic properties and to provide practical elastomers. The crosslinking approaches utilized in the fluorinated systems are based either on inherent crosslinking sites (as present in vinylidene fluoride-perfluoropropene copolymers) or in the case of hydrogen-free compositions on the presence of functional groups introduced by copolymerization with a suitable monomer, ¹⁻⁴ which is necessitated by the chemical inertness of perfluorinated materials.

It thus would seem that in the case of the relatively inert fluorinated polymers, as exemplified by $-(CF_2)_n-$, $-[CF_2CF_2CF_2CF(CF_3)]_n-$, $-[CF(CF_3)CF_2O]_n-$, and $-[(CF_2)_xO]_n-$ compositions, the introduction via copolymerization of a functional comonomer amenable to a predetermined cure offers the most plausible approach. On the other hand, in view of the work done by Davis and Merkl ^{5,6} and also in view of the "etching" ⁷ of Teflon the concept of C-C bond formation using an active agent needs to be explored as a possible avenue for curing perfluoroalkyl and perfluoroalkylether materials.

The current program included both of the above approaches, namely the synthesis of functional monomers useful for copolymerization with nonfunctional moieties and the evaluation of potential agents capable of curing nonfunctional perfluorinated systems. Triphenyl phosphine was one of the promising materials investigated by Davis and Merkl ^{5,6} in their studies of perfluoropropene-tetrafluoroethylene copolymers. In view of this finding and the known affinity of phosphorus for fluorine, the crosslinking studies performed under this program consequently were concentrated on substituted phosphines, whereas functional perfluorinated epoxides were the candidate moieties investigated for preparing curable perfluoroalkylether based compositions.

II. DISCUSSION

The absence of hydrogen and unsaturation renders perfluorocarbons and perfluoroalkylether polymers relatively inert to chemical attack and thus not readily amenable to chemical cure. Consequently, to obtain a crosslinkable material the preferred route both in perfluorocarbons and perfluoroalkylethers would seem to be the incorporation into the polymer chain of pending functional groups via the use of suitable comonomers. Yet, there are observations reported which tend to indicate that the crosslinking of fluorocarbons using organometallic or organometalloid compounds or metals offers a certain promise.⁵⁻⁷ Whether this type of action can be extended to perfluoroalkylether based materials needs to be proven since the presence of oxygen in the polymer backbone may have a significant effect on the reactive behavior towards such cross-linking agents.

Both of these crosslinking approaches were pursued under the present program and for ease of presentation will be discussed in separate subsections.

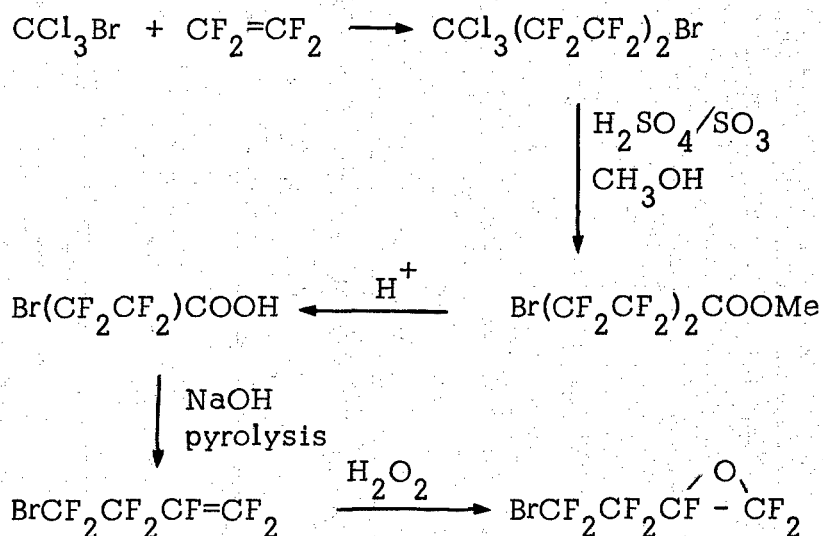
1. Synthesis of Functional Monomers

Introduction of a functional group into a perfluoroalkylether system offers one of the avenues to obtaining a curable polymer. The perfluoroalkylether systems are produced by metal fluoride catalyzed telomerizations; thus any potential monomer must contain an epoxy moiety and the functional group must remain unaffected during the polymerization process. Anderson⁴ solved this problem by the use of epoxides containing an olefin linkage. The disadvantage of this approach was the synthesis of the monomer which as the last step in the synthesis sequence required dehalogenation of the epoxide. Since epoxides are susceptible to nucleophilic attack and are hydrolyzed even by water⁸ any transformations of the oxide itself

lead invariably to low yields of the desired monomer.

The path chosen under the current program was the preparation of a bromo-terminated epoxide. The synthesis scheme is presented below.

SCHEME I



The free radical catalyzed telomerization of tetrafluoroethylene with bromotrichloromethane to $\text{Cl}_3(\text{CF}_2\text{CF}_2)_{1-4}\text{Br}$ telomers,⁹ followed by the hydrolysis to the free acid or preferentially to the ester^{10,11} has been described. No difficulty was expected in the hydrolysis of the ester to the free acid, preparation of the sodium salt, and its pyrolysis to the bromobutene. The pyrolysis reaction was carried out in 76% yield by Aldrich et al¹² using the chloro-analogue, whereas the preparation of the chloro-epoxide is described by Zapevalov.¹³

In view of the scarcity of $\text{Cl}_3\text{C}(\text{CF}_2\text{CF}_2)_2\text{Br}$, prior to initiation of the actual synthesis of the functional monomer the optimum reaction conditions for the pyrolysis and in particular for the epoxidation process

were determined employing perfluorooctanoic acid as a readily available substitute.

The sodium salt of perfluorooctanoic acid was obtained from the acid in essentially quantitative yield and, varying the pyrolysis conditions, yields of 68-88% of perfluoroheptene-1 were realized. The epoxidation procedure initially tried utilized 30% hydrogen peroxide following reported procedures.⁴ In the best reaction only 18% of the epoxide was produced which could not be isolated as pure substance but was obtained only as a 30% epoxide - 70% olefin mixture. These two compounds could not be separated by gas chromatography even using a Porapak Q column which does separate the various unsaturated isomers, e.g. perfluoro-n-heptene-1 from heptene-2. The only way to obtain the pure epoxide was via bromination of the admixed olefin, followed by vacuum fractionation. This process lowered the yield of epoxide to 9%, making this reaction totally unsuitable for the preparation of $\text{BrCF}_2\text{CF}_2\text{CF}(\text{O})\text{CF}_2$. In the majority of the epoxidation reactions only ca 50% material recovery was attained; this is attributed to rearrangement into the acid fluoride.⁸ It should be noted that the epoxide was only formed using J. T. Baker hydrogen peroxide. Mallinckrodt "30%" (in reality 32%) hydrogen peroxide did not produce any epoxide. Apparently the stabilizer present in the Mallinckrodt hydrogen peroxide (acetanilide) promoted degradation of the epoxide. Conducting the reaction with Baker's hydrogen peroxide at -10°C instead of -20°C gave only traces of the epoxide, whereas carrying out the reaction at -20° for 6 hr instead of 2 hr failed to increase the yield.

Zapevalov¹³ et al performed the epoxidation using 60% hydrogen peroxide and claimed yields of the order of 60-80%. Thus 70% hydrogen peroxide containing sodium stannate stabilizer was obtained from FMC Corporation and using this reagent yields of 60% of olefin-free epoxide

were realized. It is believed that this process can be optimized even further.

In the synthesis of the functional epoxide, $\text{BrCF}_2\text{CF}_2\text{CF}(\text{O})\text{CF}_2$ the telomerization reaction was not carried out since a mixture of telomers, $\text{CCl}_3(\text{CF}_2\text{CF}_2)_x\text{Br}$ was obtained from Dow Corning Corporation (courtesy Dr. O. Pierce). Fractionation gave the desired $\text{Cl}_3\text{C}(\text{CF}_2\text{CF}_2)_2\text{Br}$ admixed with hexachloroethane, the latter did not interfere in transformation into the methyl ester which was accomplished in 85% yield using the method of Kim et al.¹⁰ The subsequent hydrolysis into the free acid followed by the sodium salt isolation was performed in 87% yield; the olefin, $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$, was obtained in 87% yield from the sodium salt, bringing the overall yield starting from $\text{CCl}_3(\text{CF}_2\text{CF}_2)_2\text{Br}$ to 60.5%. It is expected that employing the epoxidation procedure found successful in the preparation of perfluoroheptene oxide, $\text{CF}_3(\text{CF}_2)_4\text{CF}(\text{O})\text{CF}_2$, the desired epoxide will be obtained in at least 60% yield. Considering the number of steps involved, the projected overall yield of 36% is reasonable.

2. Crosslinking Investigations of Nonfunctional Systems

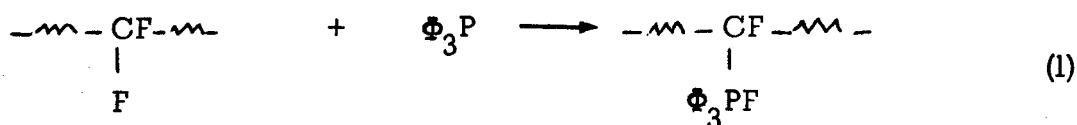
In perfluoropropene oxide derived perfluoroalkylethers, ignoring the end groups or assuming these to be a C_2F_5 entity, there are five types of bonds present. These are the $-\text{C}-\text{C}-$ and $-\text{C}-\text{O}-\text{C}-$ backbone linkages which must not be affected by the crosslinking process since their reaction would represent a degradation of the starting material. The remaining three types of bonds present are fluorine attached to a primary (CF_3), a secondary (CF_2), and a tertiary (CF) carbon atom. One of these bonds must break if a crosslink is to be produced. Taking under consideration all bond energies involved in these five types of linkages it becomes clear that the selection of the crosslinking agents and conditions is very critical. It furthermore becomes obvious that all free energy changes involving the crosslinking agent must be considered very carefully

since these may not only provide the driving force for the reaction to occur, but may actually be responsible for producing the desired reactions of C-F bonds and preventing the undesired reactions of C-C and C-O-C bonds.

Mettalloid compounds, as exemplified by $\text{Sb}(\text{C}_6\text{H}_5)_3$, $\text{Sn}(\text{C}_6\text{H}_5)_4$, and $\text{P}(\text{C}_6\text{H}_5)_3$, appeared to effect crosslinking of perfluoropropene-tetrafluoroethylene copolymer, ^{5,6} possibly via the tertiary fluorine atom; however, this has not been either proved or disproved. Based on these findings and the thermodynamic considerations put forward above it may be concluded that the most promising crosslinking agent for perfluorinated materials is a species which upon reaction with fluorine produces a large heat of formation or, in other words, where the free energy of formation of the fluoride is strongly negative in the temperature range in which the crosslinking reaction is performed. Species possessing these properties are elements or compounds capable of increasing their state of oxidation, e.g. triphenylphosphine.

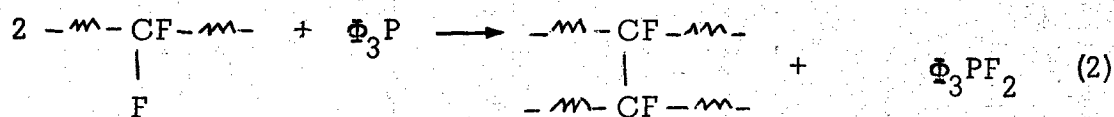
Theoretically, a compound such as triphenylphosphine may be expected to undergo either one (or both) of the following reactions:

a) abstraction of fluorine from the chain with simultaneous attachment to carbon, e.g.:



which obviously does not (at least initially) produce a crosslink, or

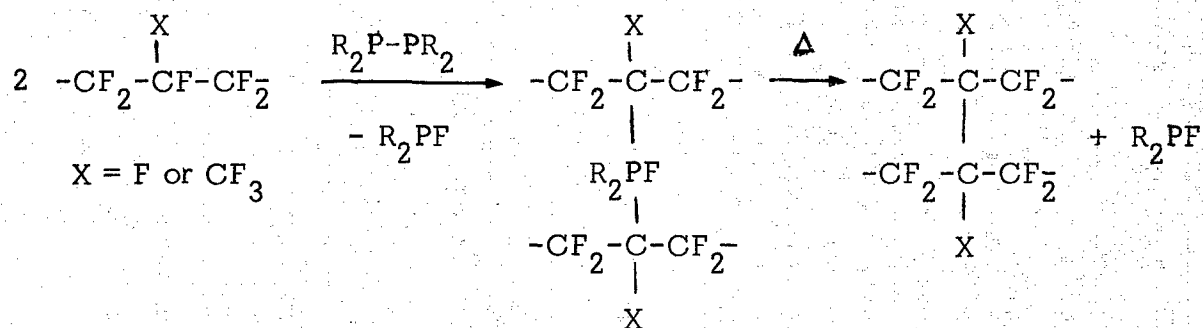
b) abstraction of fluorine with formation of the difluorophosphorane leaving two C radicals which can combine, e.g.:



For triphenylstibine it is reported, however, that phenyl groups were incorporated in the crosslink⁶ which indicates that these processes are not as simple as just depicted.

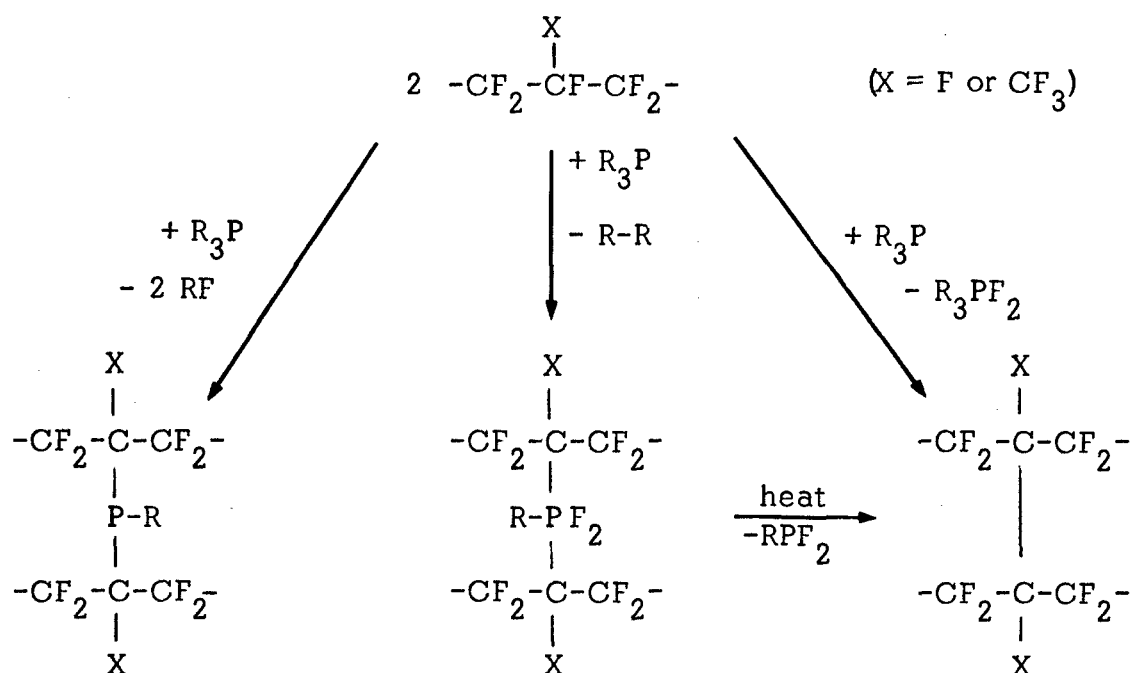
The use of subvalent compounds containing direct metal/metal or metalloid/metalloid bonds should provide a related approach. Among the many candidate subvalent compounds tetraphenyldiphosphine, $(\text{C}_6\text{H}_5)_4\text{P}_2$, offers a well known example. Two modes of attack can be visualized with any of these compositions, i.e.:

SCHEME II



or, using R_3P as an example and allowing the R-substituents to participate in the reaction, e.g.:

SCHEME III



It has to be understood that postulation of any mechanism at this stage is merely a speculation, but such an exercise at least indicates the feasibility of a particular occurrence.

The investigations conducted under this program were based on the rationale delineated above. The specific experiments are summarized in Table 1. The two crosslinking agents primarily employed were triphenylphosphine and tetraphenyldiphosphine. The fluorocarbon model compounds were selected to determine in a discriminate fashion the reactivity of the various groups and linkages under consideration towards these selected crosslinking agents, e.g. perfluorotetrahydrofuran for the presence of CF_2 groups and C-C and C-O-C linkages, perfluoromethylcyclohexane for the presence of fluorine attached to a tertiary (CF) and primary (CF_3) carbon, and the ether of composition $[(\text{CF}_3)_2\text{CFO}]_2(\text{CF}_2)_4$ for the simultaneous presence of all linkages and arrangements

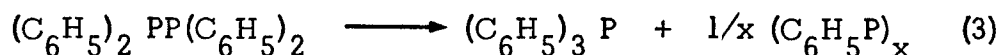
TABLE I
SUMMARY OF THERMAL CROSSLINKING INVESTIGATIONS

Model Compound		Crosslinking Agent		Temp	Time	Model Compd Recovery	Crosslinking Agent Recovery
Type	mg	Type	mg	°C	hr	%	%
-	-	(C ₆ H ₅) ₃ P	732.4	300	24	-	100
-	-	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	1041.0	300	24	-	a
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2-\text{O}}$	589.7	-	-	300	24	100.0	-
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2-\text{O}}$	321.8	(C ₆ H ₅) ₃ P	373.2	300	24	99.7	100
$\overline{\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2-\text{O}}$	578.1	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	999.0	300	24	99.4	b
c-C ₆ F ₁₁ (CF ₃)	978.1	-	-	300	24	99.8	-
c-C ₆ F ₁₁ (CF ₃)	981.2	(C ₆ H ₅) ₃ P	731.1	300	24	93.1	70
c-(C ₆ F ₁₁)CF ₃	991.1	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	966.3	300	24	81.7	c
c-(C ₆ F ₁₁)CF ₃	1958.2	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	1030.0	200	192	98.1	100
c-(C ₆ F ₁₁)CF ₃	1728.7	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	1017.7	250	113	95.3	d
[(CF ₃) ₂ CFO] ₂ (CF ₂) ₄	998.4	-	-	300	24	99.9	-
[(CF ₃) ₂ CFO] ₂ (CF ₂) ₄	3030.7	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	976.9	250	42	99.5	e
[(CF ₃) ₂ CFO] ₂ (CF ₂) ₄	2843.6	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	946.4	300	24	100.0	b
c-(C ₆ F ₁₁)CF ₃ ^f	4120.0	(C ₆ H ₅) ₂ PK	1040.0	25	168	93.3	n.a. ^g
c-(C ₆ F ₁₁)CF ₃ ^f	3840.0	(C ₆ H ₅) ₂ PK	1040.0	90	13	96.0	n.a. ^g
c-(C ₆ F ₁₁)CF ₃	4061.1	(C ₆ H ₅) ₂ PK	1075.2	154	24	96.3	n.a. ^g
-	-	(C ₆ F ₅) ₂ PP(C ₆ F ₅) ₂	542.0	300	24	-	100
c-(C ₆ F ₁₁)CF ₃	964.5	(C ₆ F ₅) ₂ PP(C ₆ F ₅) ₂	1238.9	300	24	97.6	100
Benzoxazole ^h	512.2	-	-	300	24	99.5	-
Benzoxazole ^h	2190.2	(C ₆ H ₅) ₂ PP(C ₆ H ₅) ₂	791.5	300	24	75.4	n.a. ^g

a) Based on (C₆H₅)₃P isolated by sublimation the disproportionation (see equation 3) occurs to 77%. b) The disproportionation products were found in the same ratio as in a). c) Based on (C₆H₅)₃P produced the disproportionation process took place to ~50% of that observed in the absence of c-C₆F₁₁(CF₃) (a). d) Based on (C₆H₅)₃P produced the disproportionation process took place to the extent of 1%. e) Based on (C₆H₅)₃P produced the disproportionation process took place to the extent of 5.5%. f) This test was performed under nitrogen by-pass. g) The residual phosphorus compound was not analyzed. h) The benzoxazole studied was Compound I.

considered. The selection of 300°C as the upper temperature was dictated by previous studies.⁶

Each crosslinking agent and the model compound had to be subjected individually to the temperature contemplated for the crosslinking reaction to determine the thermal stability of the materials involved and to ascertain the absence of purely thermal effects. Inspection of Table 1 reveals that all model compounds and crosslinking agents were stable at 300°C with the exception of tetraphenyldiphosphine which underwent disproportionation to an extent of 77% according to



This rearrangement proceeds most likely via an intermediate free radical, $(\text{C}_6\text{H}_5)_2\text{P}^\cdot$, which may be expected to be an active fluorine abstractor.

Interaction of perfluorotetrahydrofuran with triphenylphosphine and tetraphenyldiphosphine resulted in the quantitative recovery of the fluorinated material; triphenylphosphine was also recovered quantitatively and in the case of tetraphenyldiphosphine, the extent of transformation according to equation (3) was identical to that observed for this compound in the absence of the perfluoroalkylether. From these results it is obvious that neither of these phosphorus compounds degrades or reacts with a $-\text{CF}_2\text{CF}_2-\text{O}-$ arrangement under the conditions employed.

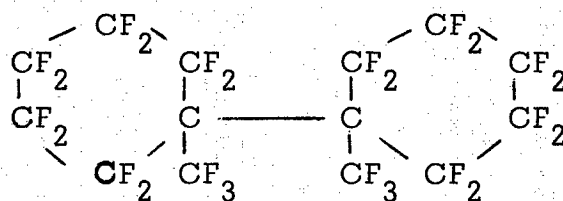
The effect of these reagents on a material containing a tertiary fluorine was examined next. Based on the 93% recovery of the perfluoro-(methylcyclohexane) employed and in view of the unambiguous identification of the products formed in the interaction with triphenylphosphine (see Table 2), it is clear that this compound was affected by the phosphine.

TABLE 2
VOLATILE PRODUCTS OBTAINED ON INTERACTION OF
TRIPHENYLPHOSPHINE AND PERFLUORO(METHYLCYCLOHEXANE)

Compound	mg	%
CF_3H	0.02	0.002 ^a
$\text{c-C}_6\text{F}_{12}$	0.01	0.001 ^a
C_6F_{14}	0.03	0.003 ^a
$\text{c-C}_6\text{F}_{11}(\text{CF}_3)$	912.9	93.05 ^a
$\text{C}_7\text{F}_{11}\text{H}$	1.84	0.19 ^a
C_6H_6	0.27	0.037 ^b
PF_3	0.03	0.004 ^b
SiF_4	14.0	1.43 ^a
$\text{C}_6\text{H}_5\text{F}$	T	T

- a) The percentages are given with respect to perfluoro(methylcyclohexane) originally employed.
b) The percentages are given with respect to triphenylphosphine originally employed.

Unfortunately, this process failed to give the desired coupled product:



It should be noted that the sublimation of the involatile residue at 60-110°C resulted in the recovery of ca 70% of $(\text{C}_6\text{H}_5)_3\text{P}$. In the sublimes obtained at the higher temperature was also found $(\text{C}_6\text{H}_5)_3\text{PO}$, identified by mass spectral analysis, corresponding to ca 9% of triphenylphosphine originally employed. The formation of the oxide (in an air-free system) in conjunction with the isolation of silicon tetrafluoride would tend to

indicate that $(C_6H_5)_3PF_2$ was produced (compare Scheme III), which at the high temperature reacted with the silica of the Pyrex tube.

The action of tetraphenyldiphosphine at $300^\circ C$ was even more drastic as is apparent from the lower starting material recovery and the increased formation of products, both in type and in quantity (see Table 3).

TABLE 3
PRODUCTS OBTAINED ON INTERACTION OF
TETRAPHENYLDIPHOSPHINE AND PERFLUORO(METHYLCYCLOHEXANE)
AT $300^\circ C$ FOR 24 HR

Compound	mg	%
$c-C_6F_{11}(CF_3)$	809.7	81.7 ^a
$C_7F_{11}H$	T	T
C_6H_6	8.9	0.7 ^b
$C_6H_5(CH_3)$	T	T
PF_3	14.8	3.1 ^b
SiF_4	55.0	4.1 ^a
$C_6H_5PF_2O$	7.3	0.8 ^b
$(C_6H_5)_2PFO$	302	25.7 ^b
$(C_6H_5)_2PF$	T	T
$(C_6H_5)_2PH$	T	T
$(C_6H_5)_3P$	259.2	26.1 ^{b,c}

a) The percentages are given with respect to perfluoro(methylcyclohexane) originally employed. b) The percentages are given with respect to tetraphenyldiphosphine originally employed. c) When tetraphenyldiphosphine is transformed at $300^\circ C$ by itself, this value was found to be 53%.

As can be seen from Table 3, GC-MS analysis definitely revealed the presence of phosphine oxides amongst the reaction products. Yet the infrared spectrum of the involatile reaction residue, from which these oxides were separated via GC, did not indicate the presence of phosphine oxides. It must be mentioned, however, that this interpretation of the infrared spectrum is based on comparison with the spectra of similar type compounds since the infrared spectrum of $(C_6H_5)_2PFO$ is not readily available. (The review of Schmutzler¹⁴ which includes related compounds prepared up to 1965 does not report $(C_6H_5)_2PF$ nor $(C_6H_5)_2PFO$.) It thus cannot be ruled out that oxidation did occur on the gas chromatographic column, since all the manipulations prior to sample injection were carried out in the inert atmosphere enclosure. In addition, the GC analysis at best accounts for 60% of the residue, the nature of the remaining 40% is unknown. The GC-analysis performed on this residue using a Porapak Q column, which would be expected to separate any lower boiling perfluoro(methylcyclohexane) derived fluorocarbons, i.e., the desired coupled product, furthermore showed no trace of such materials at all. These findings, in conjunction with the recovery of only ~82% of the perfluoro(methylcyclohexane) employed, may allow the conclusion that "crosslinking" of perfluoro(methylcyclohexane) did take place to a degree but was so extensive that only high molecular weight products were formed which were retained on the GC column.

It can be deduced from the results discussed above that apparently the presence of the fluorocarbon containing a fluorine attached to a tertiary carbon atom does affect the primary products, $(C_6H_5)_2P$ radicals, of the thermal decomposition of tetraphenyldiphosphine since significant quantities of $(C_6H_5)_2PF$ species were found (in the form of $(C_6H_5)_2PFO$). It was thus hoped that use of lower temperatures for prolonged periods of time should make the process more controllable and should lead to

the desired coupled products. Conducting the reaction at 200°C for 192 hr gave an essentially quantitative recovery of the reagents. No rearrangement of tetraphenyldiphosphine took place under these conditions. At 250°C the reaction mechanism was apparently identical to that observed at 300°C (see Table 4); however, the extent of reaction was lower. The formation of $C_7F_{10}H_2$ is unexplained.

TABLE 4
PRODUCTS OBTAINED ON INTERACTION OF
TETRAPHENYLDIPHOSPHINE AND PERFLUORO(METHYLCYCLOHEXANE)
AT 250°C FOR 113 HR

Compound	mg	%
$c-C_6F_{11}(CF_3)$	1643.5	95.3 ^a
$C_7F_{11}H$	0.04	0.002 ^a
$C_7F_{10}H_2$	6.48	0.38 ^a
C_6H_6	0.91	0.09 ^b
$C_6H_5(CH_3)$	T	T
PF_3	0.42	0.04 ^b
SiF_4	6.04	0.35 ^a
$C_6H_5PF_2O$	1.0	0.10 ^b
$(C_6H_5)_2PFO$	19.1	1.76 ^b
$(C_6H_5)_2PF$	T	T
$(C_6H_5)_3P$	5.1	0.50 ^b

a) The percentages are given with respect to perfluoro(methylcyclohexane) originally employed.

b) The percentages are given with respect to tetraphenyldiphosphine originally employed.

Perfluoro(methylcyclohexane), being a cyclic compound, could exhibit a reactive behavior due to steric effects not present in a linear arrangement. Accordingly, the perfluoroalkylether model, $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$, which also contains fluorine bonded to a tertiary carbon atom, was prepared from a $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{I}$ precursor. This material was thermally stable at 300°C and at 250°C appeared to be susceptible to fluorine abstraction by tetraphenyldiphosphine, as indicated by the data given in Table 5. However, no coupled product or products were found.

TABLE 5
PRODUCTS OBTAINED ON INTERACTION OF
TETRAPHENYLDIPHOSPHINE AND $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$
AT 250°C FOR 42 HR

Product	mg	%
$(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$	3015.0	99.5 ^a
$\text{C}_6\text{H}_5\text{PF}_2\text{O}$	T	T
$(\text{C}_6\text{H}_5)_2\text{PFO}$	31.8	3.21 ^b
$(\text{C}_6\text{H}_5)_2\text{PF}$	T	T
$(\text{C}_6\text{H}_5)_3\text{P}$	29.2	2.95 ^b

a) The percentages are given with respect to $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$ originally employed.

b) The percentages are given with respect to tetraphenyldiphosphine originally employed.

The extent of reaction at 300°C was comparable to that observed at 250°C insofar as fluorinated phosphorus compounds were concerned and the amount of triphenylphosphine found agreed well with that produced in the absence of the fluorocarbon (see Table 6). Thus it must be assumed that $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$ is unreactive

TABLE 6
PRODUCTS OBTAINED ON INTERACTION OF
TETRAPHENYLDIPHOSPHINE AND $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$
AT 300°C FOR 24 HR

Product	mg	%
$(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$	2844	100.0 ^a
CO_2	0.32	0.01 ^a
SiF_4	0.11	0.004 ^a
C_6H_6	0.86	0.09 ^b
$(\text{C}_6\text{H}_5)_2$	T	T
$(\text{C}_6\text{H}_5)_2\text{PFO}$	13.6	1.44 ^b
$(\text{C}_6\text{H}_5)_3\text{P}$	508.0	53.7 ^b

a) The percentages are given with respect to $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$ originally employed.

b) The percentages are given with respect to tetraphenyldiphosphine originally employed.

towards tetraphenyldiphosphine and triphenylphosphine (the latter being one of the thermal rearrangement products of tetraphenyldiphosphine). The small quantities of fluorinated phosphines found (Tables 5 and 6) originate most likely from the impurities present in the perfluoroalkylether, which is not surprising in view of the difficulties encountered in its purification. The apparent discrepancy between the results obtained at 250°C and 300°C, i.e. a 100% recovery of the model compound at the higher temperature compared with a 99.5% recovery at the lower temperature, in addition to the formation of higher amounts of $(\text{C}_6\text{H}_5)_2\text{PFO}$ at 250°C, is readily explained. The sample subjected to the 300°C treatment was the material recovered from the 250°C reaction and was therefore of higher purity because the trace impurities originally present

were destroyed to a considerable extent during the 250°C exposure to tetraphenyldiphosphine.

Concerning all the models studied, the failure of phosphines to effect a significant degree of fluorine abstraction with concomitant formation either of coupled or unsaturated products could have been due to the fact that at all test temperatures employed the fluorinated species were present exclusively in the gas phase. Accordingly, the investigation of a perfluorocarbon with a vapor pressure at 300°C in the vicinity of 1 atmosphere became necessary. The E-fluids represent such a series of materials and, although not ideal for model studies in view of the multiple $-\text{CF}(\text{CF}_3)-$ linkages present (under extensive crosslinking conditions gelation would result), are adequate to ascertain the stipulations advanced above.

The specific fluid employed for these investigations was E-7 fluid and its composition is given in Table 7. The conditions of the reactions performed utilizing this fluid are summarized in Table 8 whereas the characterization or rather composition of the E-fluid after the various treatments is presented in Tables 9 and 10. The data given in the two tables is the same, but differently expressed. This has been done because it is very difficult to accurately measure the fluid and deliver it to a GC column since in view of its involatility it has to be injected via a 6" long needle. The form of presentation used in Table 10 affords results which are independent of the quantity of material introduced.

The first test at 300°C was carried out to determine the thermal stability of the fluid in the absence of reactants. The other two tests were conducted to evaluate the action of tetraphenyldiphosphine. It is clearly evident from the data given in Tables 9 and 10 that no significant degradation nor crosslinking did take place in any of these experiments. If any crosslinking had taken place, additional peaks with significantly

TABLE 7

GAS CHROMATOGRAPHIC ANALYSIS OF EL066-55, FREON E-7 (c) FLUID^a

RT min	Area/ μ l	Peak Identification
1.5	1.9	$C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_3)H$
3.5	7.0	$C_3F_7O[CF(CF_3)CF_2O]_3CF(CF_3)H$
5.9	13.9	$C_3F_7O[CF(CF_3)CF_2O]_4CF(CF_3)H$
8.2	17.2	$C_3F_7O[CF(CF_3)CF_2O]_5CF(CF_3)H$
10.3	22.7	$C_3F_7O[CF(CF_3)CF_2O]_6CF(CF_3)H$
12.4	18.4	$C_3F_7O[CF(CF_3)CF_2O]_7CF(CF_3)H$
13.6	4.8	$C_3F_7O[CF(CF_3)CF_2O]_8CF(CF_3)H$
14.9	1.3	$C_3F_7O[CF(CF_3)CF_2O]_9CF(CF_3)H$
16.1	0.5	$C_3F_7O[CF(CF_3)CF_2O]_{10}CF(CF_3)H$
17.4	0.2	$C_3F_7O[CF(CF_3)CF_2O]_{11}CF(CF_3)H$

a) The conditions used: Column: stainless steel
 10' x 1/8" 1% OV-17 on Chromosorb G-AW; column effluent
 split 10% into F.I., remainder into TC detector; He flow:
 35 ml/min; column temperature: 50-220°C programmed at 8°/min.

TABLE 8

SUMMARY OF EL066-55, FREON E-7(c) FLUID REACTIONS

Freon E-7 g	$(C_6H_5)_4P_2$ g	Temp °C	Time hr	Remarks
1.0607	none	300	24	No noncondensibles formed; GC essentially identical with starting material.
2.9603	1.0944	247	264	No noncondensibles formed; GC of fluorinated layer essentially identical with starting material.
3.3270	1.0118	300	24	No noncondensibles formed; GC of fluorinated layer essentially identical with starting material.

TABLE 9
GAS CHROMATOGRAPHIC ANALYSIS^a OF ELO 66-55, FREON E-7(c) FLUID
(Area/ μ l After Various Heat Treatments)

RT min	(As Received)	(300°C, 24 hr)	(247°C, 264 hr, plus Φ_4P_2)	(300°C, 24 hr plus Φ_4P_2)
1.5	1.9	1.7	1.4	1.8
3.5	7.0	8.8	7.3	9.5
5.9	13.9	12.6	11.5	16.4
8.2	17.2	14.3	14.2	22.6
10.3	22.7	24.5	21.6	27.3
12.4	18.4	17.5	15.2	19.3
13.6	4.8	4.3	3.4	4.6
14.9	1.3	1.2	1.0	1.3
16.1	0.5	0.5	0.3	0.5
17.4	0.2	0.2	0.1	0.2

a) The conditions used: Column: stainless steel 10' x 1/8" 1% OV-17 on Chromosorb G-AW; column effluent split 10% into F.I., remainder into TC detectors; He flow: 35 ml/min; column temperature: 50-220°C programmed at 8°C/min.

TABLE 10
GAS CHROMATOGRAPHIC ANALYSIS OF ELO 66-55, FREON E-7(c) FLUID
(Area as Percent of Largest Peak After Various Heat Treatments)

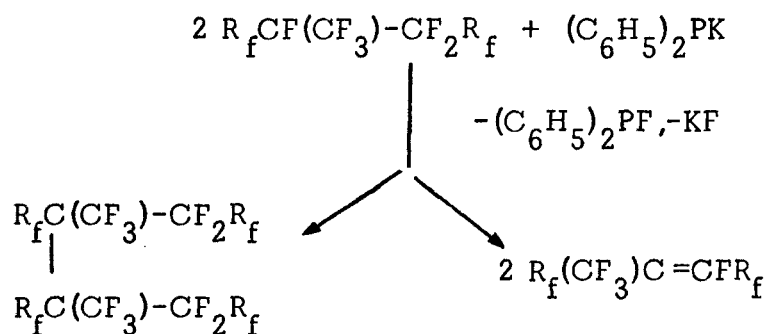
RT min	(As Received)	(300°C, 24 hr)	(247°C, 264 hr plus Φ_4P_2)	(300°C, 24 hr plus Φ_4P_2)
1.5	8.1	7.9	6.2	6.6
3.5	31.7	43.6	33.5	35.0
5.9	61.3	55.7	52.9	60.3
8.2	75.9	70.8	65.8	82.8
10.3	100	100	100	100
12.4	80.9	76.6	70.3	70.7
13.6	21.1	18.9	15.6	16.9
14.9	5.9	5.5	4.5	4.8
16.1	2.3	2.1	1.5	1.7
17.4	0.9	0.7	0.4	0.6

longer retention times would have been observed and for the earlier peaks lower area/ μ l values would have been registered. This would be also portrayed by higher percentages of the latter peaks with respect to the 100% peak and these ratios would differ greatly from those of the untreated E-fluid.

At this stage of the investigation, two conclusions could be drawn: The phenyl substituted phosphines are ineffective in fluorine atom abstraction at temperatures up to 300° due (a) to insufficiently negative free energy changes produced by the contemplated reactions (b) to the fact that the reagents are mutually insoluble and immiscible, which is enhanced by the large density differences between fluoro-carbon and crosslinking agent.

A potential crosslinking agent combining an alkali metal and a phosphine character is potassium diphenylphosphide, $(C_6H_5)_2PK$. It was believed that this material should readily effect the abstraction of a tertiary fluorine at moderate temperatures since the formation of potassium fluoride should thermodynamically be favored. Such a reaction should produce either an unsaturated or a coupled product, i.e.:

SCHEME IV



No reaction was observed on treatment of perfluoro(methylcyclohexane) with potassium diphenylphosphide at room temperature even after prolonged periods of time. The nonquantitative starting material recovery (93%) is attributed to sample loss during the addition of the phosphide to an open flask in the inert atmosphere enclosure. A similar reason is advanced for the 96% material recovery, after the exposure to 85-90°C, inasmuch as here the reaction was carried out under a nitrogen by-pass. At 154°C, decomposition of potassium diphenylphosphide occurred as shown by the black, charred residue. Yet, 96% of the fluorocarbon was recovered unchanged and only traces of products derived from the fluorinated reagent were found (see Table 11).

TABLE 11
PRODUCTS OBTAINED ON INTERACTION OF
POTASSIUM DIPHENYLPHOSPHIDE WITH PERFLUORO
(METHYLCYCLOHEXANE) AT 154°C

Compound	mg	%
c-C ₆ F ₁₁ (CF ₃)	3909.5	96.26 ^a
C ₆ H ₆	8.35	0.78 ^b
SiF ₄	0.023	0.001 ^a
CO ₂	0.215	0.005 ^b
PF ₃	T	T
H ₂	0.069	0.006 ^b

a) The percentages are given with respect to c-C₆F₁₁(CF₃) employed. b) The percentages are given with respect to potassium diphenylphosphide employed.

Accordingly, one is forced to conclude that even having the alkali metal combined in the phosphine moiety does not provide an effective fluorine abstracting agent.

The apparent lack of reaction of tetraphenyldiphosphine and the other phosphorus compounds with the fluorinated compositions could be, as noted above, due to the mutual insolubility of these systems.

The investigation of perfluorinated phosphines was thus undertaken. Bis(pentafluorophenyl)chlorophosphine was prepared in 45% yield via reaction of pentafluorophenylmagnesium bromide with phosphorus trichloride. Using elemental mercury, the coupling to the desired diphosphine was accomplished in essentially quantitative yield. Subjecting tetrakis(pentafluorophenyl) diphosphine to heat treatment in vacuo at 300°C for 24 hr (see Table 1) resulted in dark discoloration and production of 2.2 mg (0.4% of starting material) of volatiles which were composed of C_6F_5H , PF_3 , CO_2 , and a trace of C_6F_6 . The hydrogen in pentafluorobenzene originated most likely from traces of heptane and benzene which were employed to crystallize tetrakis(pentafluorophenyl)diphosphine. Prior to reaction, the sample was dried for 22 hr at 60°C and had mp 183.5-185°C. The dark discolored residue (after the heat treatment) had mp 141-148°C; however, its infrared spectrum was identical with that of the starting material. Gas chromatography failed to show even traces of $(C_6F_5)_3P$. Based on the above, it has to be deduced that up to 300°C $(C_6F_5)_2PP(C_6F_5)_2$ does not undergo the disproportionation observed for its hydrocarbon analogue (compare equation 3). This finding was not encouraging insofar as crosslinking of perfluoro(methylcyclohexane) is concerned; however, it was believed possible that in the presence of both compounds a reaction might take place. As can be seen from the data given in Table 1 no reaction occurred.

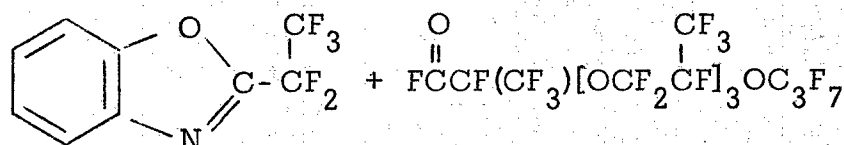
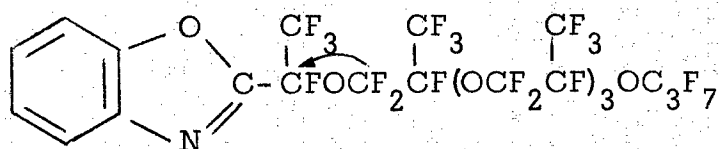
[illegible]O=C1C(=O)N(C1)c2ccccc2

23

TABLE 12
PRODUCTS OBTAINED ON INTERACTION OF
 $\text{RCF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_4\text{OC}_3\text{F}_7$ AND $(\text{C}_6\text{H}_5)_4\text{P}_2$

Compound ^a	mg	%
$\text{R}-\text{CF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_4\text{OC}_3\text{F}_7$	1650.862	75.37
$\text{R}-\text{CF}(\text{CF}_3)[\text{OCF}_2\text{CF}(\text{CF}_3)]_2\text{OC}_3\text{F}_7$	0.980	0.04
$\text{R}-\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	0.420	0.02
$\text{R}-\text{CF}(\text{CF}_3)\text{OC}_3\text{F}_7$	0.121	0.01
$\text{R}-\text{CF}(\text{CF}_3)\text{H}$?	2.435	0.11
$\text{R}-\text{CF}_2\text{CF}_3$	5.236	0.24
$\text{R}-\text{CF}_3$	0.960	0.04
$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_4\text{CF}(\text{CF}_3)\text{H}$	0.280	0.01
$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{CF}_2\text{H}$	0.964	0.04
$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_3\text{CF}(\text{CF}_3)\text{H}$	85.030	3.88
$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}(\text{CF}_3)\text{CF}_2\text{H}$	6.531	0.30
$\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}(\text{CF}_3)\text{H}$	42.101	1.92
$\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{H}$	2.907	0.13
$\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{H}$	23.562	1.08
$\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{H}$	1.385	0.06
$\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{H}$	6.659	0.30
C_3F_6	0.335	0.02
$\text{CF}_3\text{CF}_2\text{H}$	0.392	0.02
C_6H_6	0.855	0.11 ^b
$\text{C}_6\text{H}_5\text{CH}_3$	0.067	0.01 ^b
$\text{C}_6\text{H}_5\text{PF}_2\text{O}$	5.017	0.63 ^b
$(\text{C}_6\text{H}_5)_2\text{PFO}$	225.336	28.47 ^b
CO	4.732	0.22
CO_2	15.27	0.70
PF_3	8.41	0.38
SiF_4	129.21	5.90

a) R = benzoxazole ring. b) These percentages are given with respect to tetraphenyldiphosphine; all the other values are based on the benzoxazole originally employed.



Hydrolysis of the acid fluoride by water on the glass walls, followed by thermal decarboxylation would thus explain the formation of $\text{HCF}(\text{CF}_3)-[\text{OCF}_2\text{CF}(\text{CF}_3)]_3\text{OC}_3\text{F}_7$. This mechanism would also explain the presence of the other benzoxazoles listed in Table 12, which were definitely absent in the original sample. The quantity of carbon monoxide liberated (0.17 mmol) corresponds to approximately 1/3 of the benzoxazole reacted. In view of the type of products isolated, it would seem that the CO originates from the benzoxazole ring. If one considers all the fluorinated products found and since these account for the major weight percent of the benzoxazole, it is evident that 1/3 of the material loss is unaccounted for. This material is apparently a part of the charred Freon and benzene insoluble residue.

Apparently the reaction between the benzoxazole and the $(\text{C}_6\text{H}_5)_2\text{P}^\cdot$ radicals originating from tetraphenyldiphosphine proceeded very readily since the "normal" rearrangement product, triphenylphosphine, could not be detected and 28% of tetraphenyldiphosphine was transformed to $(\text{C}_6\text{H}_5)_2\text{PFO}$. It was noted in past discussion that most likely the originally produced $(\text{C}_6\text{H}_5)_2\text{PF}$ is oxidized to $\text{C}_6\text{H}_5\text{PFO}$ during gas chromatography. Based on the results obtained, it would seem that at lower temperatures, ca 250°C , the process could be better controlled

and might lead to crosslinking since, compared to the "straight" perfluoroalkylethers, the presence of the benzoxazole ring provides definite activation. The question remains whether this activation can lead to crosslinking or whether it only offers a facile degradation path.

III. EXPERIMENTAL DETAILS AND PROCEDURES

1. General

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectrometric analyses were obtained employing CEC Model 21-620 instrument and a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

2. Material Purification and Characterization

The crosslinking investigations were performed at high temperatures and thus it was imperative to eliminate any side reactions due to impurities. Traces of impurities which could not be removed readily by conventional means were identified and quantitated and their effect during thermal and crosslinking studies noted.

a. Perfluorotetrahydrofuran

Perfluorotetrahydrofuran was received from AFML; it was synthesized by the 3M Company Research Department. Roughly 1500 cm³

(STP) of this material was introduced into a standard high vacuum line, containing mercury manometers and mercury float valves. The material, as introduced, had a vapor pressure at -78° (VP_{-78}) of ≈ 23 mm. It was fractionated from a warming trap through traps kept at -78 , -96 , -112 , and -196°C . The -78° trap contained a small amount of a material, $VP_{-78} = 7.8$ mm; the -96° and the -112° traps contained almost equal amounts of material with -78° vapor pressures of 7.5 and 9.6 mm, respectively. The -96 and -112° fractions were recombined and refractionated using the above procedure. The -78° fraction thus obtained was negligibly small, the -96° fraction ($\approx 2/3$ of the total sample) had a $VP_{-78} = 7.7$ mm and showed an infrared spectrum almost identical to that published for $\text{C}_4\text{F}_8\text{O}$; ¹⁵ but this material did exhibit weak absorption in the CH region (3.3μ). The molecular weight of this fraction, using the gas density method, was found to be 216 (theory 216.03). However, GC-MS of this fraction (see Figure 1), (employing a stainless steel, 8' x 1/8" Porapak Q column, flame ionization detector, with a 47% split into a DuPont spectrometer 491B, He flow: 35 ml/min; temperature, $50-220^{\circ}\text{C}$ programmed at $7^{\circ}\text{C}/\text{min}$) showed the presence of several impurities. Based on the mass spectral patterns of the GC peaks (retention times given in brackets) the largest GC peak is composed essentially of perfluorotetrahydrofuran (base peak, m/e 100) admixed with some CH material ($m/e = 51$); the remainder of the gas chromatographic peaks are composed predominately of CH-containing species as indicated by $m/e = 51$ being the 100% peak. This -96°C fraction was employed in the subsequent investigations.

b. Triphenylphosphine

Triphenylphosphine was a Matheson, Coleman and Bell product and was sublimed in vacuo, mp $80-81^{\circ}\text{C}$.

PLOT GC			
GC ID AA	10	DATE	3/ 3/76
AQRATE	6	SCTIME	2
HIMASS	500	THRESH	2
		RESPWR	500

PERFLUOROTETRAHYDROFURAN

% F.S.	100	REZERO	YES	SEQUEN	33
BASE	21589	*2** 5			

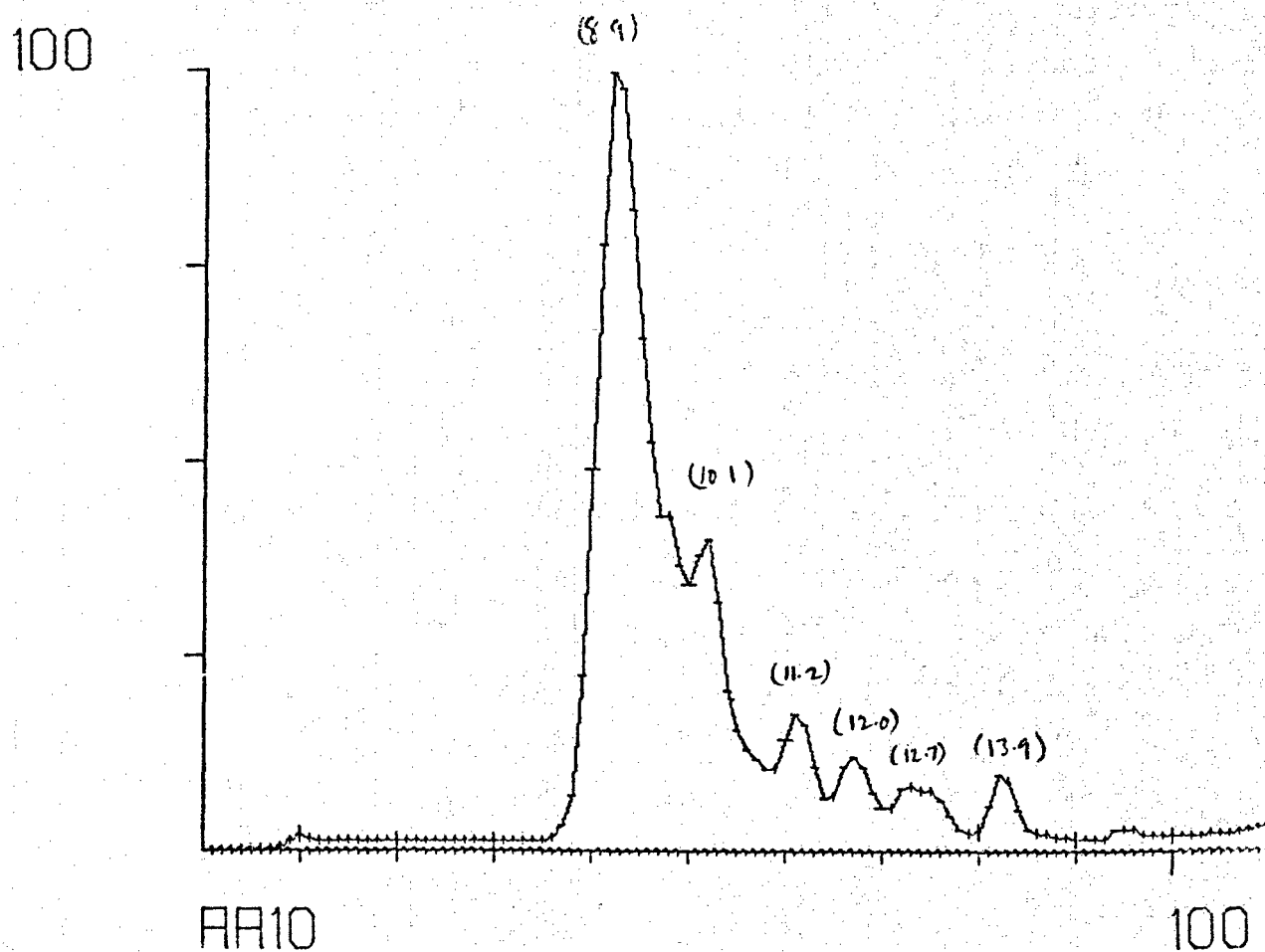


Figure 1. GC-MS Trace of Perfluorotetrahydrofuran

c. Perfluoro(methylcyclohexane)

Perfluoro(methylcyclohexane), purchased from PCR, Inc., was fractionated in vacuo from a warming trap through traps kept at -47, -63, -78, and -196°C. The -47°C and the -63°C traps contained almost equal amounts of liquid. The -63°C fraction, ($VP_0 = 29.6$ mm) was subjected to GC-MS analysis employing a stainless steel, 8' x 1/8" Porapak Q column with a 43% split into a DuPont spectrometer 491B, He flow: 35 ml/min; temperature, 50-200°C programmed at 7°C/min. Based on the GC and GC-MS traces (see Figure 2) and peak printouts the sample is almost pure perfluoro(methylcyclohexane) (rt, 18.3 min) mixed with traces of perfluorohexane, perfluorocyclohexane (both rt, 16.1 min) and dimethyl (perfluorocyclohexane) (rt. 21.9 min). This fraction was employed in subsequent investigations.

d. Tetraphenyldiphosphine

The tetraphenyldiphosphine was prepared in 71% yield, mp 126-127°C, via interaction of diphenylphosphine and diphenylchlorophosphine following the procedure of Kuchen and Buchwald.¹⁶

e. Freon E-7(c)(ELO66-55)

Based on the DTA curve (see Figure 3) Freon E-7 has a boiling point above 250°C. The broadness of the endotherm indicates that it is a multi-component mixture. The composition of Freon E-7 is given in Table 7, wherein the area/ μ l represents fairly well the relative percentage of a given homologue (the total adds up to 88% by weight). It should be noted that up to peak No. 4 (MW, 1116) the components could be identified readily using GC-MS, the major peak being M-117 (C_2F_4OH); beyond that the assignment was based on retention times and general breakdown patterns.

PLOT GC
 GC ID AA 5 DATE 4/ 1/76
 AGRATE 6 SCTIME 2 RESPWR 500
 HIMASS 500 THRESH 2
 -63 IR 5629 PERFLUOROMETHYLCYCLOHEXANE LIQ PQ
 % F.S. 100 REZERO YES SEQUEN 12
 BASE 26352 *2** 6

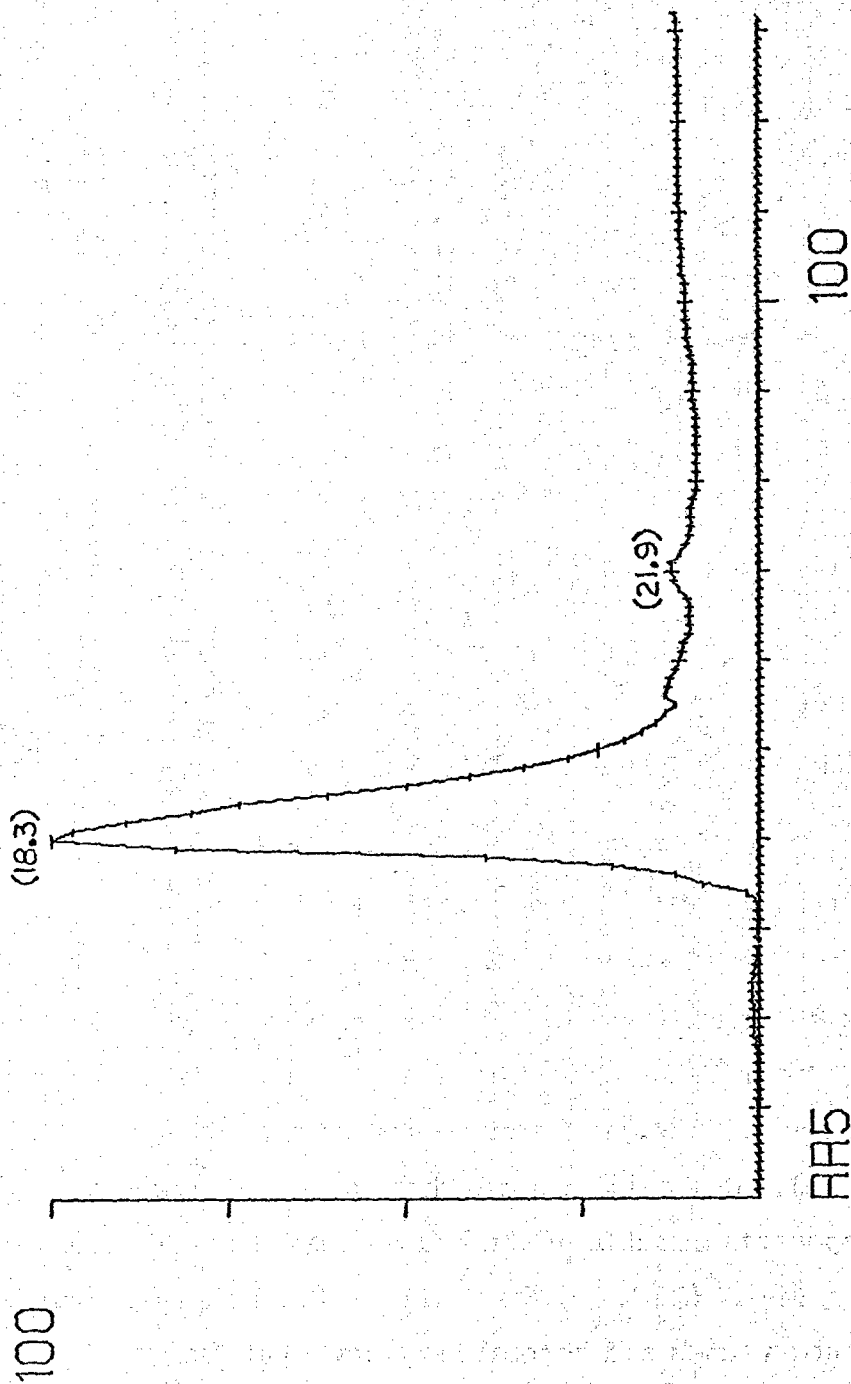


Figure 2. GC-MS Trace of Perfluoro(methylcyclohexane) (-63°C fraction)

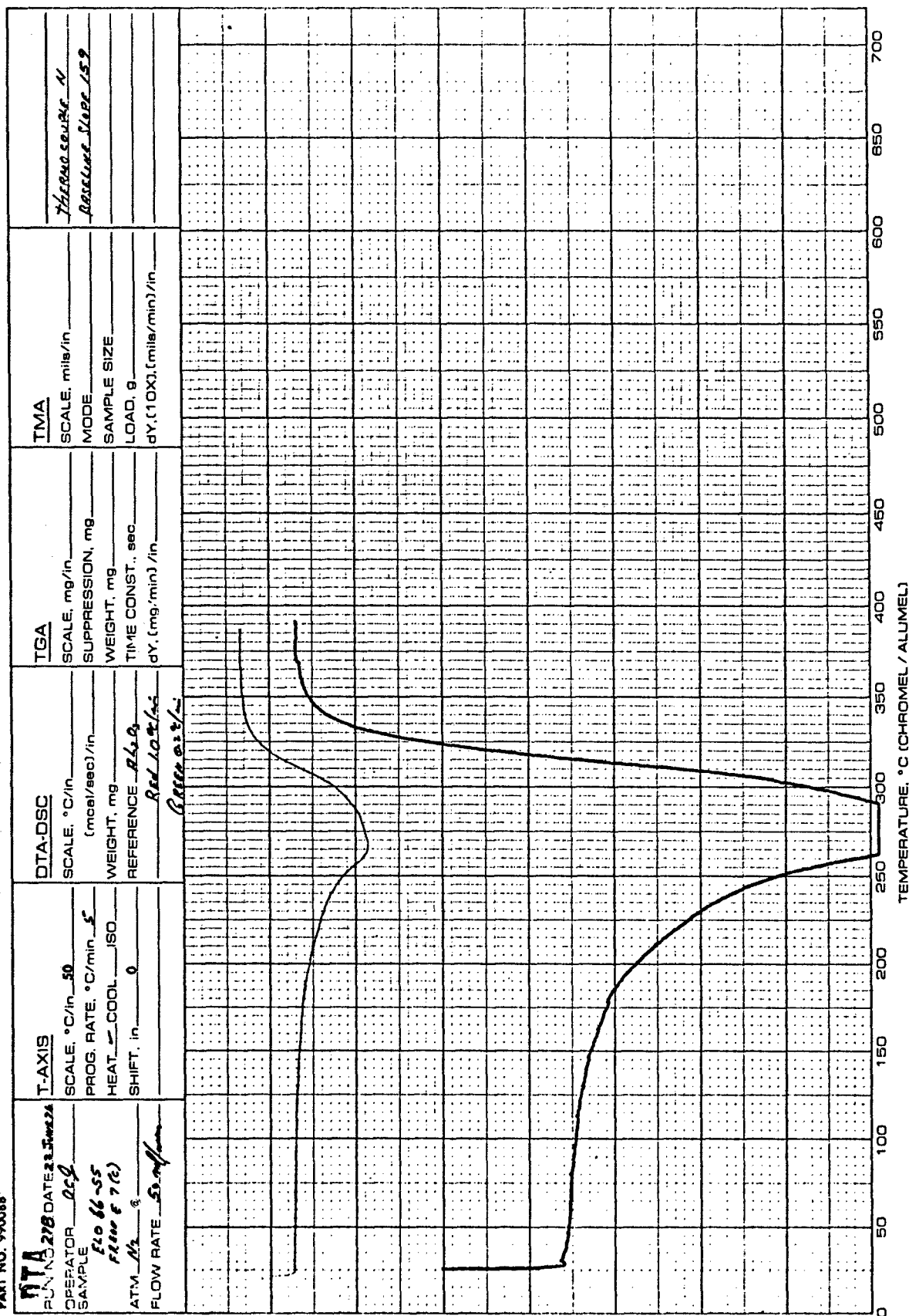


Figure 3. DTA of Freon E-7 (c) (ELO66-55)

3. Monomer and Model Compound Synthesis

a. Preparation of $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$

Following the procedure of Evers¹⁷ a mixture of the iodide, $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{I}$ (24.3 g, 59.1 mmol; 99.9% pure by GC analysis) 40 mesh zinc (12.0 g, 183.9 mmol), acetic anhydride (36.1 g, 353.7 mmol) and 1,1,2-trichlorotrifluoroethane (90 ml) were heated under a nitrogen atmosphere at reflux temperature (ca 54°C) with stirring for a period of 24 hr. During this time a white precipitate was formed. The reaction mixture was cooled, filtered and the filtrate was hydrolyzed by addition of water. The organic layer was separated out, washed with 10% sodium bicarbonate and water, dried, and distilled using a 65 mm column packed with glass helices. The fraction distilling at 40-48°C contained the Freon 113; the material collected subsequently, bp 77-94°C (7.0 g) was found by GC-MS to consist of 89% of the desired product and ca 11% of Freon 113. The pot residue contained 1.2% of Freon 113. Fractionation using a 130 mm helices packed column failed to separate the two constituents. The 77-94°C distillate (the boiling point for the coupled product is reported by Allied Chemical Corporation to be 135°C) plus the pot residue (3.24 g) amounted to 59% yield of the product. The Freon 113 content could be lowered to 0.07% by repeated vacuum line fractionation as described below; however, the product did contain also 0.8% of a perfluoroalkyl ether-acetate derivative as determined by GC-MS using Porapak-Q column programmed from 50-220°C at 8°C/min.

Passage through an alumina (GC-grade, 80/60 mesh) column (40 mm long, i.d. 10 mm) in vacuo failed to purify the material. Thus the liquid was taken up in a small quantity of Freon 113, washed with 10% sodium bicarbonate and water, dried over MgSO_4 and fractionated in vacuo through traps held at -23, -47, -78 into -196°C. The -23 and -47°C fractions were combined and refractionated as above; this process

was repeated four times. The final -23°C fraction ($\text{VP}_{25.8^{\circ}\text{C}} = 7.9 \text{ mm}$) used in the subsequent studies consisted of $(\text{CF}_3)_2\text{CFO}(\text{CF}_2)_4\text{OCF}(\text{CF}_3)_2$, 99.81% pure, and contained 0.07% of Freon 113.

b. Preparation of bis(pentafluorophenyl)chlorophosphine

Pentafluorophenylmagnesium bromide was prepared by Grignard exchange between bromopentafluorobenzene and ethylmagnesium bromide following essentially the procedure of Tamborski and Moore.¹⁸ Thus under nitrogen by-pass an ethereal solution (61.1 ml, 100.9 mmol) of ethylmagnesium bromide (the concentration was determined using high vacuum techniques by measuring the ethane produced upon hydrolysis) was added at 0°C to a stirred solution of pentafluorobromobenzene (26.53 g, 107.43 mmol) in ether (60 ml) over a period of 4 min. Subsequently the solution was stirred at room temperature for 1 hr. It should be noted that the exchange equilibrium was attained after 1 min; no change in the relative proportion of pentafluorobromobenzene and the pentafluorophenylmagnesium bromide (as determined by hydrolysis to pentafluorobenzene) was observed after the additional hour at room temperature.

The interaction of pentafluorophenylmagnesium bromide with phosphorus trichloride was performed using the procedure of Tesi, et al.¹⁹ Accordingly, under nitrogen by-pass to a stirred, ice cooled solution of phosphorus trichloride (6.94 g, 50.53 mmol) in ether (50 ml) was added the above prepared pentafluorophenylmagnesium bromide over a period of 1 hr. After addition was completed the solution was filtered in an inert atmosphere enclosure to free it from the precipitated salts, and the ether was removed in vacuo at room temperature. A yellow oil remained which was distilled using a 100 mm long column packed with glass helices. The first two fractions: 1.98 g, bp $50-60^{\circ}\text{C}/0.001 \text{ mm}$ and 3.87 g, bp $60-92^{\circ}\text{C}/0.001 \text{ mm}$ contained mainly pentafluorophenyl-dichlorophosphine; the third fraction, 9.13 g (45.2% yield) bp $92-112^{\circ}\text{C}/$

0.001 mm, consisted essentially of the desired product. Redistillation using the same column afforded pure bis(pentafluorophenyl)chlorophosphine (6.80 g, 34% yield) bp, 92-94°C/0.001 mm.

From the first distillation was recovered 2.85 g (10.7%) of bromopentafluorobenzene which condensed in a trap cooled to -78°C; based on the infrared spectrum of the ethereal distillate it also contained some bromopentafluorobenzene which amounted to 3.0 g as determined by gas chromatography. Thus the total bromopentafluorobenzene recovered added to 5.85 g (21.57 mmol); this would then indicate that the efficiency of Grignard exchange was of the order of 85%.

c. Preparation of Tetrakis(pentafluorophenyl)diphosphine

Following the procedure of Ang and Miller,²⁰ bis(pentafluorophenyl)chlorophosphine (3.12 g, 7.79 mmol) was stirred in an inert atmosphere enclosure with elemental mercury (16.37 g, 81.61 mmol) for 5 days. During that period a white solid was deposited which prevented further stirring. The organic product was taken up in boiling benzene and from the filtrate after evaporation of benzene 2.65 g (93% yield) of product was obtained. Crystallization from benzene-heptane gave tetrakis(pentafluorophenyl)diphosphine (2.00 g, 70.4%) mp 183-185.5°C; lit 165-170°C,²⁰ 159-163°C.²¹

Anal. Calcd. for: $C_{24}F_{20}P_2$: C, 39.48; F, 52.04; P, 8.48.

Found: C, 39.25; F, 51.75; P, 8.33.

In view of the elemental analysis and in particular based on infrared spectrum, absence of absorption in the 8.0-8.7 μ region, the presence of oxide can be excluded and thus the higher than to date reported melting point is most likely due to a purer product.

d. Preparation of n-Perfluoroheptene-1

The sodium salt of n-perfluorooctanoic acid was obtained in 96% yield from the acid. Pyrolysis of the salt at 241-325°C was carried out in a 100 ml round bottom flask attached to a vacuum system via two traps cooled to -78°C followed by three liquid nitrogen cooled traps. The olefin was collected in the traps cooled to -78°C. It was purified by vacuum fractionation from a warming trap through -47, -78 into -196°C cooled traps. The desired product was collected in the -47 and -78°C traps. As shown by gas chromatographic analysis the material consisted of 92-94% of n-perfluoroheptene-1, 0.5-1% of n-perfluoroheptene-2; the remainder were hydrogen-containing materials, i.e. $C_7F_{13}H$.

Three runs were carried out. These are summarized in Table 13. Run No. 3 afforded the lowest yield of the products although the conditions used were almost identical with those employed in run No. 2 with the exception that somewhat higher temperatures were employed.

TABLE 13
SUMMARY OF $n-C_7F_{15}COONa$ PYROLYSIS EXPERIMENTS

Run No.	$n-C_7F_{15}COONa$ (g)	Temperature (°C)	Time (hr)	Yield (%)
1	7.26	241-287	1.25	94
2	20.12	210-300	2.00	88
3	20.52	225-325	5.75	72

e. Epoxidation of n-Perfluoroheptene-1

i) Using 30% H_2O_2

To a mixture of $\text{n-C}_5\text{F}_{11}\text{CF}=\text{CF}_2$ (2.73 g, 7.8 mmol), 30% H_2O_2 (70.8 mmol) and methanol (3.25 ml) cooled to -23°C was added methanolic potassium hydroxide (1.28 g, 19.4 mmol dissolved in 3.6 ml methanol). The resulting mixture was stirred for 4 hr at -23 to -10°C , then transferred to a separatory funnel. The organic layer was separated and washed with cold water (3 x 10 ml) and dried over anhydrous MgSO_4 . Distillation yielded a clear liquid (1.86 g) which was shown by infrared spectroscopy to be a mixture of 67.5% starting olefin (1.26 g) and 32.5% epoxide (0.60 g, 21.2% yield).

This reaction was carried out utilizing J. T. Baker's "30%" hydrogen peroxide. Mallinckrodt "30%" (in reality 32%) hydrogen peroxide employed under the same conditions as those given above did not produce any epoxide. Apparently the stabilizer present in the Mallinckrodt hydrogen peroxide (acetanilide) promoted degradation of the epoxide. Conducting the reaction with Baker's hydrogen peroxide at -10°C instead of -20°C gave only traces of the epoxide; whereas carrying out the reaction at -20° for 6 hr failed to increase the yield.

The pure epoxide was isolated by stirring the olefin/epoxide mixture (1.70 g) with bromine (0.2 ml, 0.59 g, 3.66 mmol) at 0°C for 3 hr. The resulting mixture was transferred to a separatory funnel and washed with a saturated solution of sodium thiosulfate (4 x 10 ml) and water (3 x 5 ml), then dried over anhydrous MgSO_4 . Distillation in vacuo gave a yellowish liquid (1.32 g) which was separated via vacuum fractionation from a warming trap through traps kept at -47 , -78 and -196°C . The bulk of material, namely the 1,2-dibromoperfluoroheptane (1.02 g), was condensed in the -23°C trap.

The -78°C trap contained 0.23 g of material which was composed of 95% of n-perfluoroheptene oxide and 5% of the olefin; bringing the oxide yield as based on the olefin originally employed to 9%. This result shows clearly the inadequacy of this process.

ii) Using 60% H_2O_2

To a mixture of n-perfluoroheptene-1 (2.00 g, 5.71 mmol), methanol (1.15 ml) and 60% H_2O_2 (1.6 ml, 36.07 mmol, prepared by the dilution of 70% H_2O_2 obtained from FMC Corporation), cooled to -20°C , was added dropwise a potassium hydroxide solution (0.90 g, 13.63 mmol dissolved in methanol). The resulting mixture was stirred for 4 hr while maintaining the temperature between -20 and -14°C . At the end of the reaction period the mixture was transferred to a separatory funnel and the lower organic layer separated, then washed with ice cold water (2 x 10 ml) and dried with anhydrous magnesium sulfate. High vacuum transfer afforded a clear liquid (1.05 g) which based on its infrared spectrum, contained 4.5% of the starting olefin and 95.50% of the desired epoxide (1.00 g, 48%). The mass spectrum of the epoxide is given in Table 14.

A number of runs were conducted using the 60% hydrogen peroxide; these are summarized in Table 15. It is apparent from the data listed that for larger samples of the olefin longer reaction times are necessary to assure completeness of reaction.

f. Preparation of $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{CO}_2\text{Me}$

The starting material, $\text{Cl}_3\text{C}(\text{CF}_2\text{CF}_2)_2\text{Br}$, received from Dow Corning Corporation, (157 g) was twice distilled using a 10 cm column packed with glass helices affording 49.7 g of material, bp, $107-109^{\circ}\text{C}/133$ mm Hg. Based on gas chromatography performed using $10' \times 1/8''$ column packed with 1% OV-17 on Chromosorb G-AW 80/100

TABLE 14
ION FRAGMENTS AND INTENSITIES RELATIVE TO BASE
PEAK OF n-PERFLUOROHEPTENE OXIDE^a

m/e	%	m/e	%
31	40.0	112	7.8
47	16.0	113	2.7
50	24.1	119	30.1
59	2.1	131	64.3
69	<u>100</u>	132	6.5
70	4.0	147	5.7
74	2.6	150	2.0
78	2.0	162	5.4
81	16.8	169	16.9
93	16.3	181	25.6
97	18.4	219	2.6
100	33.8	231	25.1
101	2.5	269	5.2
109	4.0	347	2.2

a) Peaks having intensities less than 2% of the base peak are not reported.

TABLE 15
EFFECT OF REACTION PERIOD ON COMPLETENESS
OF THE EPOXIDATION PROCESS

Test No.	n-C ₇ F ₁₄ (g)	React. Period (hr)	Total Product (%) ^a	Olefin Content (%) ^b	Epoxide Yield (%) ^c
10	2.00	4	53	4.5	48
11	2.00	2	65	8.2	55
12	10.00	4	75	32.8	48
13	7.5 ^d	6	61	none	61

a) Weight percent of recovered organic material with respect to starting material used. b) The olefin content is based on infrared absorption at 5.55 μ . c) Based on originally employed olefin. d) The material used here is the total product recovered in the preceding test.

mesh, programmed at $6^{\circ}\text{C}/\text{min}$ from 40 – 220°C , the distillate consisted of $\sim 85\%$ of $\text{Cl}_3\text{C}(\text{CF}_2\text{CF}_2)_2\text{Br}$ admixed with $\sim 14\%$ of Cl_3CCl_3 and 0.6% of the lower homologue $\text{Cl}_3\text{CCF}_2\text{CF}_2\text{Br}$. Four more impurities were present in trace quantities (less than 0.25%) only. The boiling points of hexachloroethane and $\text{Cl}_3\text{C}(\text{CF}_2\text{CF}_2)_2\text{Br}$, based on the literature, appear to be almost identical preventing the separation by distillation; however, the presence of hexachloroethane did not interfere with the preparation of $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{CO}_2\text{Me}$.

Following the procedure of Kim, et al.¹⁰ to a stirred mixture of 85% pure $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{CCl}_3$, (21.08 g , 52.92 mmol), Hg_2SO_4 (0.21 g , 0.41 mmol) and HgSO_4 (1.07 g , 3.59 mmol) was added 30% oleum (19 ml) over a period of 15 min . Subsequently, the mixture was heated under reflux and nitrogen by-pass for 160 hr at 124 – 125°C . The cooled solution was then added dropwise over a period of 40 min to methanol (40 ml) stirred in an ice-bath. This was followed by stirring at room temperature for an additional 15 hr . The methanolic solution was added into 90 ml of ice and water. A clear organic layer (13.36 g) separated at the bottom. This was composed of 98% of the desired ester. The supernatant aqueous solution and an emulsion that had formed at the interphase of the two layers were extracted with ether and the extract dried with magnesium sulfate and distilled in vacuo followed by fractionation from a warming trap through traps held at 0° , -23 , -47 into -196°C . The material present in the -23 and -47°C traps (1.83 g) was also composed of 98% of the ester $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{COOMe}$. Thus the total yield of the ester based on $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{CCl}_3$ employed was 84.7% , in good agreement with the results of Kim, et al.¹⁰

g. Preparation of $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{CO}_2\text{Na}$

Sodium hydroxide (2.59 g , 64.75 mmol) was dissolved in water (65.6 ml). To the warm solution was added dropwise $\text{BrCF}_2\text{CF}_2^-$

$\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ (13.78 g, 40.65 mmol) over a period of 10 min. The resulting mixture was stirred at ambient temperature for 5 days. The alcohol was subsequently removed under reduced pressure and the solution acidified with concentrated sulfuric acid (2 ml). The solution was then subjected to continuous ether extraction over a period of 8 days. Removal of ether by distillation followed by evaporation in vacuo yielded a slightly orange liquid (12.72 g, 96.1% yield) whose mass spectral analysis indicated the ester to be present in 1.5%. Titration with 0.4526 N sodium hydroxide to pH 7.05 followed by drying gave 12.32 g (87.4% yield based on the ester) of the sodium salt $\text{Br}(\text{CF}_2\text{CF}_2)_2\text{COONa}$.

h. Preparation of $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$

The sodium salt, $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{Na}$ (12.23 g, 35.25 mmol), was heated under vacuum at 268–300°C for 4.0 hr. The reaction was carried out in a 100 ml round bottom flask attached to a vacuum system via three liquid nitrogen cooled traps. The product, which collected mainly in the first liquid nitrogen cooled trap, was purified by vacuum fractionation from a warming trap through -63, -78, -96 into -196°C cooled traps. Fractions -63 (3.79 g) and -78°C (1.49 g) contained 98 and 95% pure $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$, respectively, the other components being $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$, $\text{CF}_2=\text{CFCF}=\text{CF}_2$, $\text{CF}_2\text{HCF}_2\text{CF}=\text{CF}_2$, $\text{ClCF}_2\text{CF}_2\text{CF}=\text{CF}_2$, $\text{BrCF}_2\text{CF}=\text{CFCF}_3$ and $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$. The fractions -63 and -78°C thus added to 5.12 g, 55.7% yield of the olefin, $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$. The pyrolysis residue (5.63 g) based on its infrared spectrum still contained the original sodium salt, $\text{CF}_2\text{BrCF}_2\text{CF}_2\text{CF}_2\text{COONa}$; accordingly, the pyrolysis process was repeated giving in the -63 and -78°C fractions 2.00 and 0.96 g of product respectively, equal to an additional 2.87 g of the pure olefin. The total weight, 7.99 g, of the olefin thus obtained corresponds to 87% yield (based on the sodium salt employed). The overall yield of the desired olefin starting from $\text{Cl}_3\text{CCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{Br}$ is thus 60.5%. The mass spectrum of the olefin, $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$ is given in Table 16.

TABLE 16
ION FRAGMENTS AND INTENSITIES RELATIVE TO
BASE PEAK OF $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2^a$

m/e	%	m/e	%
31	18.4	131	<u>100</u>
50	5.8	132	12.1
62	3.4	162	15.7
69	22.3	181	12.2
74	4.9	191	16.5
79	2.5	193	16.2
81	11.7	241	1.9
93	23.8	243	1.8
100	8.0	260	11.8
112	13.9	262	11.6
129	12.5		

a) Peaks having intensities less than 2% of the base peak are not reported; however, m/e 241, 243 have been included since these are M-19 ions.

4. Crosslinking Studies

The thermal investigations were performed in evacuated sealed ampoules of ca 25 ml volume over the specified period of time and at the denoted temperatures (see Table 1). At the conclusion of an experiment the ampoules were cooled in liquid nitrogen, and were opened to the vacuum system. The liquid nitrogen noncondensibles, if produced, were measured with the aid of a Sprengel pump and determined by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were fractionated from a warming trap through traps kept

at -23 , -78°C into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy and gas chromatography/mass spectrometry. The residue itself was weighed and subjected to GC-MS, infrared spectral analyses, and differential thermal analysis.

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